MECHANISMS OF CHROMIUM EMISSIONS FROM WOOL FIBERGLASS GLASS-MELTING FURNACES

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WOOL FIBERGLASS MANUFACTURING

The Wool Fiberglass Manufacturing source category includes any facility engaged in producing wool fiberglass from sand, feldspar, sodium sulfate, anhydrous borax, boric acid or any other materials. In the wool fiberglass manufacturing process, molten glass is formed into fibers which may then be bonded with an organic resin to create a wool-like material that is used as thermal or acoustical insulation. The category includes, but is not limited to the following processes: glass-melting furnace, marble forming, refining, fiber forming, binder application, curing and cooling.

FURNACE TECHNOLOGIES

One wool fiberglass manufacturer provided the EPA with general schematics of the four different furnace types used to produce wool fiberglass. In general, these are electric furnaces (including both cold-top electric and electric steel shell) and gas-fired furnaces (including both oxyfuel and air-gas). [1]

The industry is capable of producing a variety of products on any type of furnace, however, the current general industry trend is to manufacture residential insulation on rotary spin lines which are fed by gas-fired furnaces, and high density fiberglass products on flame attenuation lines which are fed by either electric or gas-fired furnaces. Higher density products typically have a lower production rate in order to achieve both a higher volume of fiberglass per cubic foot and greater amount of resin application to that fiberglass volume. Electric furnaces are generally more suited to that production rate, although the production line fed by a gas-fired furnace can be designed to also produce higher density products.

CHROMIUM REFRACTORIES

Chromium as chromite (Cr_2O_3) is added to refractories to provide superior resistance to both thermal and chemical attack.

"Refractory materials are chemical compounds that are used as structural materials forming insulation linings and/or as containment vessel in high temperature and corrosive environments in many industrial processes. The use of chromium in refractories is second in importance to its metallurgical applications. The mineral chromite is the only ore of chromium. About 15% of the total world chromite consumption is from the refractories industry." [2]

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[1] Mike Pettis, Owens Corning, Inc. in response and follow-up to site visits conducted at wool fiberglass manufacturing facilities, December 2012.

[2] According to the EVISA website, "The European Virtual Institute for Speciation Analysis is a service provider in the fields of speciation analysis. EVISA's web portal is the primary source for all those seeking information about chemical species with respect to analysis, biological activity (toxicity, nutritional value, metabolism), legislation (laws, rules, standards) and research in related fields."

ANH Refractories writes in their website[3], "Wool and C-Glass[4] makers rely on NARCO's extensive line of chrome-alumina materials, the SERV and JADE brands, available in standard pressed brick, large cast shapes, and Cast-in-Place linings."

In 2012, the EPA requested under authority of section 114 of the Clean Air Act (CAA), chromium (total and hexavalent) emissions testing and furnace construction data of all operating glass-melting furnaces located at wool fiberglass facilities in the U.S. This CAA section 114 Information Collection Request (ICR) included questions to obtain information about the chromium content of all refractories based on location in the furnace, furnace age, last rebuild and repair date, and anticipated furnace life. While the facility-specific data are confidential business information (CBI), the data characterizing the use of chromium refractories in furnace construction were averaged at each furnace location according to percent chromium in the refractory. These data are presented in Table 1 below.

According to the North American Insulation Manufacturers Association (NAIMA), "Fiber glass companies have chrome emissions because insulation glass manufacturers use refractory products that contain chrome to make up the glass furnace (*see* Attachment 8, spreadsheet showing typical chrome content). These can either be in glass contact (pavers (floor) or sidewalls) or above glass (superstructure (frontwall, backwall, and breastwalls)), along with port and stack. Insulation manufacturers use these … refractories because of the unique composition of C- Glass. C-Glass contains boric oxide (B_20_3). This oxide is essential to give the fiber necessary characteristics for its specific use. Unfortunately, boron compounds are not compatible with refractory containing alumina (Al_20_3). Alumina is a key component in just about every other major form of high temperature refractory. Since the advent of chrome based refractory, insulation manufacturers have been able to extend furnace life up to 50 percent. Without these refractories, wool fiber glass manufacturers would not likely be competitive in the global marketplace."

FUNCTION AND PURPOSE OF CHROMIUM REFRACTORY IN THE WOOL FIBERGLASS INDUSTRY

Chromite, derived from ore, is used in the material formulation for the manufacture of chromium refractories for its ability to withstand the interior fiberglass furnace environment.[5] The European Virtual Institute for Speciation Analysis (EVISA) evaluated chromium refractories in use across industry sectors, and summarizes that "Chrome-based refractories are typically used in cement kilns, secondary steel refining furnaces, foundry sands, glass melting furnaces, and incinerators. In some cases alternative materials -- such as magnesium-aluminium spinels, spinel-bonded magnesite and high alumina refractories -- have replaced chrome-containing refractories. However, these materials do not always meet performance or cost requirements."

[3] http://www.anhrefractories.com/ANH-refractories-about. ANH Refractories was formed by a merger of A.P. Green, NARCO, and Harbison-Walker in 2001.
[4] Per NAIMA, C- Glass is the generic glass chemistry designation for fiberglass insulation
[5] "Chromium in Refractories". Sept. 2000. Dr. Mariano Valez, Ceramic Engineering Dept., Univ. Missouri-Rolla.

Table 1. Percent of Chromium in Refractory by Furnace Location

Furnace Location	**Oxyfuel Furnace (% chromium)**	**Air Gas Furnace (% chromium)**	**Notes**
Glass Contact Side Wall	30-60%	28-95%	The glass/metal line is along this wall.
Glass Contact – Floor Paving	30-80%	28-60%	Beneath the level of the molten glass.
Breast Wall	30-60%	0%	Raw material furnace feed is typically in this area.
Crown	30-50%	0-85%[a]	The interior arching 'roof' of the furnace above the glass melt.
Back Wall	30-80%	28-95%	The area at and above the outlet of the furnace where molten glass is extruded. Temperatures and corrosion are typically higher in this area.
Portneck / Stack	50-92%	0-95%	Leading to the throat of the furnace.
Throat	50-92%	50-95%	The furnace exit.

[a] Companies did not report chromium in the refractories of the crown of air-gas furnaces. However, during site visits conducted by the EPA in December 2012, one facility operating an air-gas furnace explained that the reduction in chromium emissions was due to a 'hot repair' conducted on the crown, during which the repair was made using a non-chromium refractory patching material. This company stated that the crown was constructed of high-chromium refractories.

EVISA, a service provider in the field of speciation analysis, summarizes on their website[6] that "the usefulness of chromite as a refractory is based on its high melting point of 2,180 °C (3,960 °F), moderate thermal expansion, neutral chemical behavior, and relatively high corrosion resistance. Chromite enhances thermal shock and slag resistance, volume stability and mechanical strength. In contact with iron oxide, it forms a solid solution (a homogeneous crystalline phase composed of different minerals dissolved in one another) with iron oxide and expands considerably, causing the refractory to crumble (bursting). Adding magnesia can prevent this phenomenon."

"Substitutes for chromium-containing products are available, but they sometimes have a shorter life span. Also, a substitute that works in one application may not work in another application, or the life span is significantly reduced."[7]

[6] http://www.speciation.net/

[7] From Babcock and Wilcox Plant Service Bulletin. "Refractories, Plastics, Insulation or Textiles Containing Chromium Compounds". Babcock and Wilcox is a Field Testing Service which specializes in technical advice in industrial construction.

FURNACE DESIGN

Table 2 presents a summary of the chromium test data for wool fiberglass glass-melting furnaces. The data show a significant range of chromium emissions. Available data indicate that all furnace types use high chromium refractory in some areas (see Table 1). Because chromium refractories are used at and below the level of the glass in all wool fiberglass glass-melting furnaces (as shown in Figures 1-4), all of the glass-melting furnace types have some sources that emit at very low levels. However, only gas-fired glass-melting furnaces show a potential to emit chromium at higher levels, and to form hexavalent chromium in the furnace environment due to both temperature and chemistry. The glass-melting furnace design (layout and location of chromium refractory), energy source, glass chemistry and rate of refractory corrosion are the major factors affecting chromium emissions from glass-melting furnaces.

Table 2. Range of Chromium Compound Emissions by Glass-Melting Furnace Type

Glass-Melting Furnace Type	Chromium Compound Emissions (lb/1,000 tons glass pulled)
Electric Steel Shell	0.0022 – 00.039
Cold-Top Electric	0.00078 – 0.027
Air-Gas	0.0025 – 0.96
Oxyfuel	0.011 – 3.5

ELECTRIC FURNACES

The average emissions of all metal HAP are very low for electric glass-melting furnaces. This low emission potential is inherent in the glass-melting furnace design. Electric glass-melting furnaces establish a crust on the raw material at the surface of the molten glass during the startup process. During normal operation, the electric furnaces use electrodes which are embedded below the crust and within the molten glass to maintain the temperature of the melt, while the temperature above the melt is low. Electric furnaces also have lower air flows and low turbulence above the glass melt. Therefore, the potential for metal emissions (as part of the total PM entrained in the exhaust gas) from electric glass-melting furnaces is much lower than from gas-fired glass-melting furnaces.

Electric furnaces also do not have the same potential to emit chromium as gas-fired furnaces. The maximum measured chromium emissions at an electric furnace is approximately equivalent to the minimum chromium emissions at an oxyfuel furnace. Although electric glass-melting furnaces are lined at and below the glass/metal line with chromium refractories, they are constructed using either non-chromium refractories (cold-top electric) or steel in place of refractories (electric steel shell) above the glass/metal line. This design is used because electric glass-melting furnaces operate with a dry batch cover and are tapped at the bottom or end of the glass-melting furnace to draw off the molten glass. Raw materials are constantly added to the top of the glass-melting furnace in damp form, which maintains the crust on the surface of the molten glass.

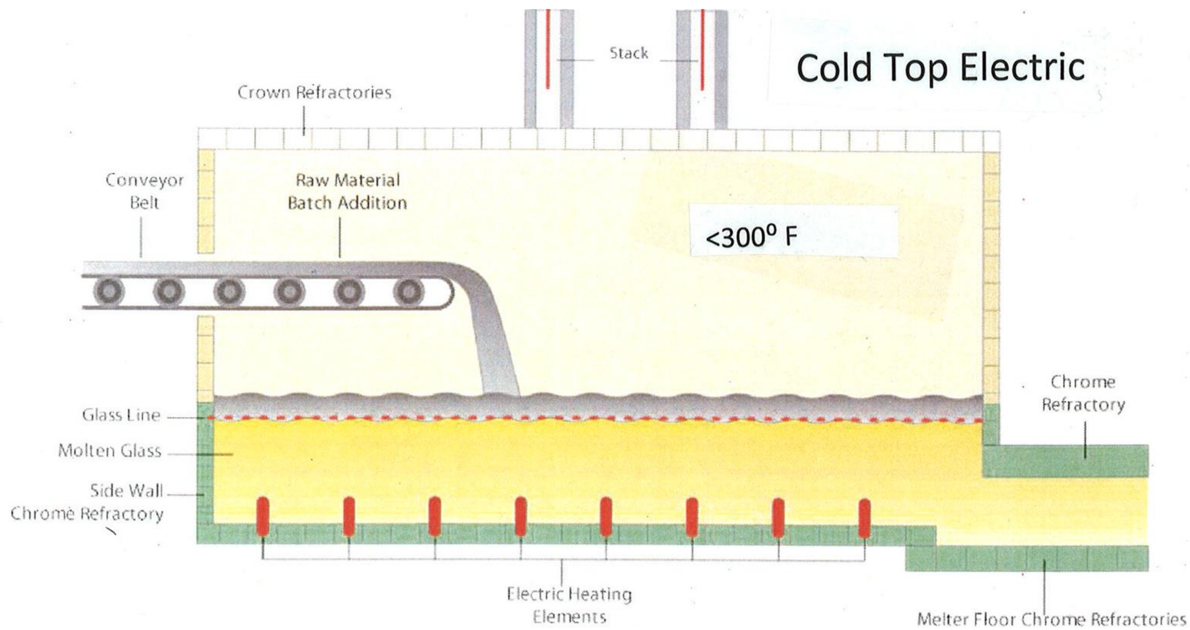


Figure 1. The Cold-Top Electric Furnace

Steel shell glass-melting furnaces have a steel enclosure above the glass/metal line and cold-top electric glass-melting furnaces use non-chromium refractories above the glass/metal line. The air above the melt inside an electric glass-melting furnace is below 300 ^{0}F, and is not hot enough to warrant use of chromium refractories. Even if chromium refractories were used to construct the crown of the electric glass-melting furnace, the temperature of an electric glass-melting furnace above the glass/metal line is insufficient to drive the chromium to its hexavalent state.

Information provided by the industry on furnace design indicates that gas-fired glass-melting furnaces have a higher potential to emit chromium compounds than electric furnaces due to the placement of the high chromium refractory, the physical layout of the furnace, the size and placement of the burners in relation to the sides and top of the glass-melting furnace, the peak flame temperature, the depth from the burners to the top of the raw materials, the temperature at and above the melt, and the oxide concentration of the glass-melting furnace gas environment. In addition, the oxyfuel furnace (the predominant type of gas-fired furnace) shows the greatest potential to convert chromium to its most toxic form, hexavalent chromium, due to the significantly higher temperature above the glass melt line of a gas-fired furnace.

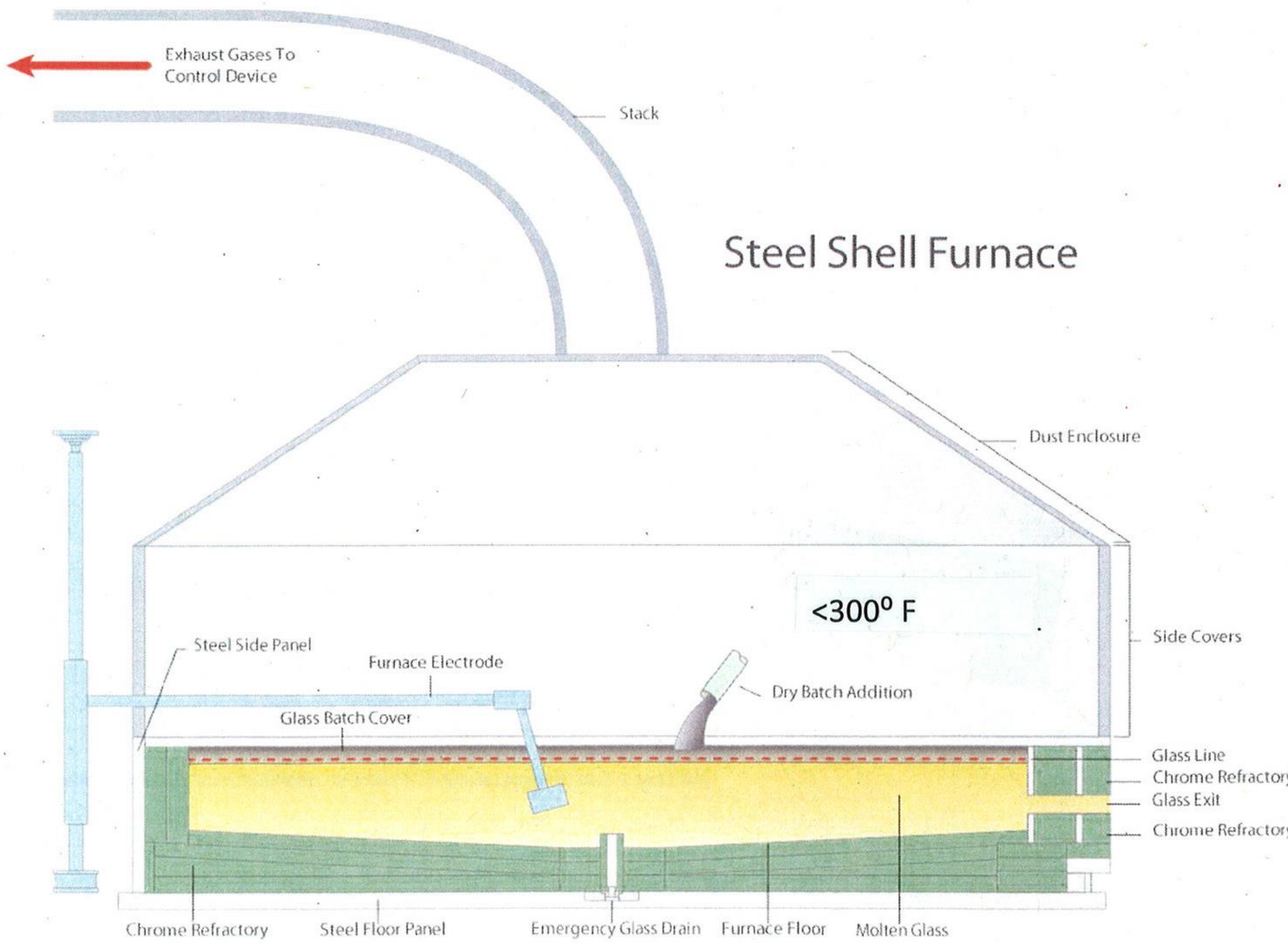


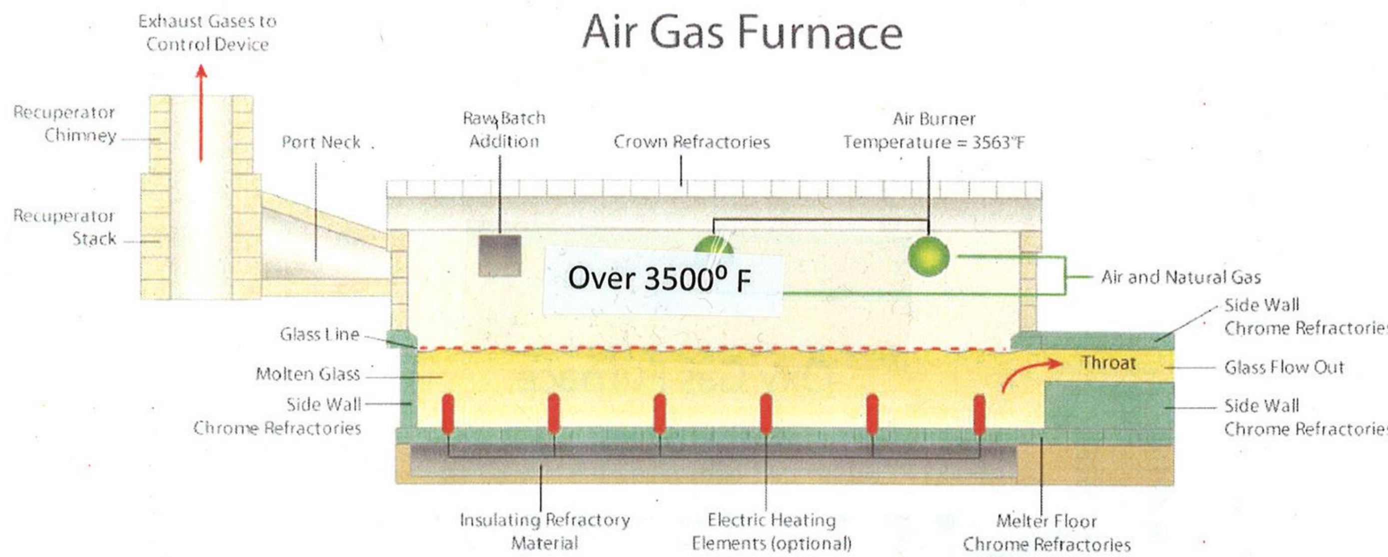
Figure 2. The Electric Steel Shell Furnace

<u>THE AIR-GAS FURNACE</u>

The data submitted by the wool fiberglass manufacturing industry on glass-melting furnace type and construction materials (in response to both NAIMA's voluntary survey and under the EPA's section 114 ICR) indicate that the highest emitting glass-melting furnace is an oxyfuel glass-melting furnace constructed using chromium refractories. However, all glass-melting furnaces with the high chromium emissions were either oxyfuel or air-gas glass-melting furnaces.

Air-gas furnaces have a higher potential to emit PM than oxyfuel furnaces because air-gas furnaces require that combustion air or oxygen and natural gas be blown into the furnace. This increases the gas flow velocities and turbulence above the glass melt line, which increases the potential for particle entrainment in the exhaust gas.

As early as the 1970's, furnace designers across the glass sector (which includes container, fibers, flat and specialty glasses) were replacing air-gas furnaces with oxyfuel technology, and expected the oxyfuel furnace to overtake the industry for the future manufacturing process[8]. By 2003, 29 percent of the air-gas furnaces at wool fiberglass insulation facilities had been replaced by oxyfuel furnace technology, and elements of furnace design, such as burner placement and crown height above the glass melt (or 'slag') were known to affect both firing rate and glass pull rates. A higher crown height results in a lower average crown refractory temperature, Figure 3. The Air-Gas Furnace



and reduces the alkali corrosion of the crown. However, as recently as 2003, the oxyfuel furnace designs still used the silica crown refractory which was known to present problems in operation at the oxyfuel furnaces, including severe corrosion at the hinges of crown bricks.[9]

ADVANTAGES OF THE OXYFUEL FURNACE

The oxyfuel furnace has numerous advantages over the air-gas furnace for the glass industry. In both furnace types, the fuel is natural gas (CH_4). Air contains 78.9% nitrogen, which acts as a ballast and reacts with oxides in the glass furnace. The combustion process in the air- gas furnace is:

$CH_4 + O_2 + N_2$ -------→ CO_2, H_2O, NOx, trace gases

The combustion process of the oxyfuel furnace is:

$CH_4 + O_2$ -------→ CO_2, H_2O, trace gases

Because only oxygen and the fuel natural gas are needed in the combustion reaction, nitrogen, which comprises almost 80% of air, is not introduced to the furnace. Several benefits are

[8] Oxyfuel Fired Glass Melting Technology – Experience, Evolution and Expectation. H. Kobayashi and A. Tasca, Praxair. Presented at the Annual Meeting of International Commission on Glass (ICG) Campos do Jord,o-SP Brazil. Sept 21-25, 2003.

[9] Severe corrosion leading to breakthrough, typically at joints and hinges of the refractory surfaces is called a 'rat hole,' or 'rat-holing.'

realized as a result of eliminating N_2 including: increased productivity, greater energy efficiency, enhanced flame stability, reduced exhaust gas volume, and reduced NOx and PM emissions.

The actual flame temperature is determined by the flame radiation efficiency and the combustion system. The best radiation efficiency occurs when both heat absorption of the load and heat refraction of the furnace walls are maximized. The combustion system is optimized when no products of incomplete combustion remain (i.e., CO and H_2 from partial combustion of CH_4, and unreacted O2 which may occur as a result of chemical dissociation, a common problem at high temperatures.)

The required fuel input is greatly reduced in the oxyfuel furnace in comparison to the air-gas furnace. The exhaust volume per unit of fuel input is reduced as a function of the elimination of nitrogen, and the available heat increases as a result of the same driver.

Productivity is increased both because of optimized heat transfer (via flame to the load) as well as the raw material substitution of cullet for all or most of the raw minerals needed to produce wool fiberglass. Because cullet is glass that has already been melted at least once, the atomic bonds of the elements of the mineral assemblages do not exist in the glass; they have already been severed in the first melting. Also in the first melting, gases such as oxygen in SiO4 (silica) and SiO2 (silicate minerals) has already been liberated, and the resulting glasses are free of those atomic bonds. They therefore melt readily and at a much lower temperature than raw minerals, the eutectic point is reached quickly, and hence the production rate is greatly increased.

Oxyfuel furnaces have much lower energy demands compared to air-gas furnaces because a portion of the heat input provided by the natural gas is not wasted in heating non-oxygen components (e.g., nitrogen) present in ambient air. In oxyfuel glass furnaces, peak flame temperatures approach 5,000 ^{o}F, whereas air-gas flame temperatures peak at about 3,560 ^{o}F.

The volume of exhaust gases is reduced significantly in the oxyfuel furnace as nitrogen is eliminated from the combustion process in the furnace. The oxyfuel furnace design achieves a large reduction in nitrogen oxides (NOx), which results from the fact that ambient air (which contains nitrogen and other compounds) is not introduced into the high-temperature zone above the glass melt. Instead, the oxyfuel glass-melting furnace design mixes the natural gas fuel with industrial-grade oxygen for combustion, thus reducing NOx emissions. The reduction in the use of outside air in the furnace greatly reduces the overall volume of furnace gases exiting the furnace stack, and hence PM emissions are greatly reduced as well.

Nitrogen also acts as a ballast in the air-gas furnace. Because it is eliminated in the oxyfuel furnace, combustion in the oxyfuel furnace is nearly complete and immediate. Management of the oxygen : natural gas mixture to raw material throughput must be closely monitored to optimize the production rate.

FURNACE MATERIALS AND DESIGN

Initially, air-gas furnaces were replaced with oxygen technology by simply adjusting the size of the ports used to inject air into the furnace, narrowing their diameter to account for the reduction in volumetric flow associated with using oxygen rather than ambient air. The balance of oxygen and natural gas in the furnace was typically also adjusted, and the aim of the oxygen flame, which is much hotter than the air-gas flame, was sometimes adjusted when possible. However, the location of the oxygen port in relation to the natural gas ports is not easily changed until the furnace rebuild. Other furnace features that require changes to the furnace design and/or gas flow through the furnace can only be added at rebuild.

The oxygen and natural gas jets in the oxyfuel furnace should be designed, aimed, and positioned to optimize the combustion process specific to each oxyfuel furnace design. Refractory corrosion is exacerbated when the flame direction is too high (i.e., aimed at the crown), the crown is too low for the furnace design, or when the flame is too robust (and impacts the opposite side of the furnace).

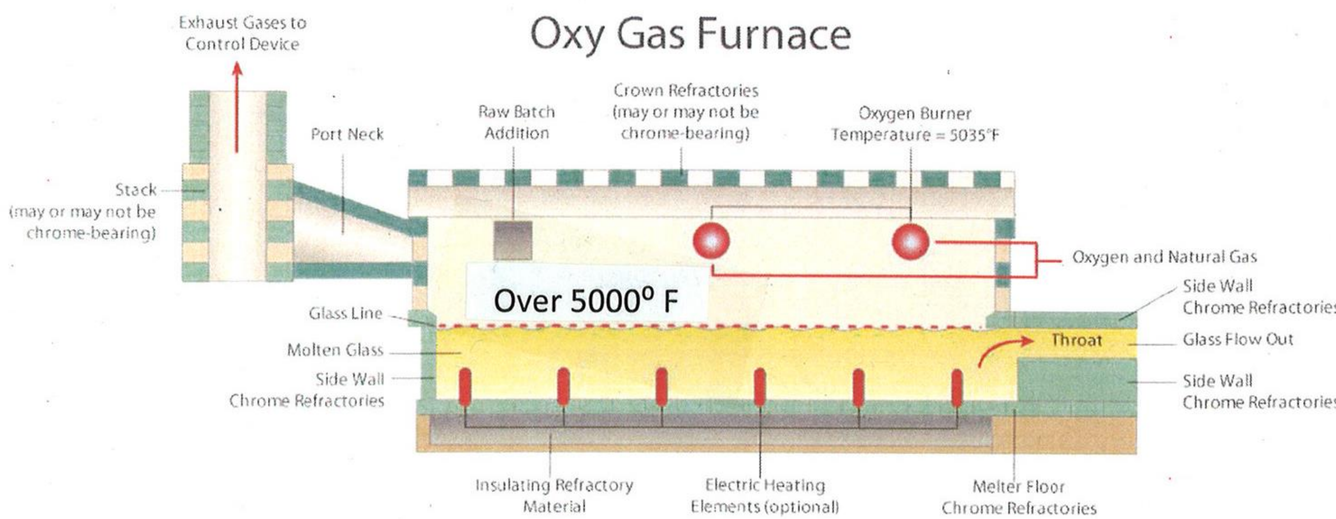


Figure 4. The Oxyfuel Furnace

The Department of Energy's (DOE's) Office of Industrial Technology, in association with persons in the glass manufacturing, refractory production sectors and the Oak Ridge National Laboratory, conducted studies to determine ways to optimize energy uses, needs and efficiencies in industrial sectors. In these studies, it was agreed that oxyfuel glass-melting furnaces will ultimately replace air-gas glass-melting furnaces by 2020 due to economic and environmental factors. Participants in the Industrial Technologies Program (ITP), under the DOE's Energy Efficiency and Renewable Energy program, described the demands an oxyfuel glass-melting furnace places upon the refractory lining: "The ITP has recognized that a reduction in overall domestic energy consumption will occur if the primary energy-consuming industries improve their own energy efficiencies. Recognizing this need, the glass industry is currently converting older, conventional air-fuel-fired furnaces to oxyfuel firing, or in the case of new construction, is building new oxyfuel-fired furnaces instead. This has caused oxyfuel technology to become one of the fastest growing technologies in the glass industry because it promises pollution abatement, increased glass-pull effectiveness, capital cost savings and increased energy efficiency. For example, a recent study has shown that approximately $202M in energy savings per year in 2005 and a $445M per year savings by 2020 could be expected with the conversion of air/fuel to oxyfuel–fired glass manufacturing furnaces. These results, which reflect energy savings of 2.8 and 14.2 TBtu/year, respectively, are based on the projection that 61 percent and 100 percent furnace conversions will occur by the years 2005 and 2020, respectively."

According to technical sources,[10, 11]once a source of reasonably priced oxygen becomes available, the oxyfuel glass-melting furnace is the design favored for use by glass manufacturers due to the advantages of oxyfuel furnaces over other glass-melting furnaces discussed above (i.e., low NOx emissions, low energy demands per volume output of glass, and high production rate, especially with the increased use of cullet in the raw material mixture).

CHROMIUM EMISSIONS AND THE GAS-FIRED FURNACE

"Unlike other fiber glass furnace classes, virtually all of the above-glass refractory in a gas-oxy furnace[12] is also chrome bearing. Currently, there is no material available that is as good as chrome based refractory to resist the chemical corrosion and have the structural integrity at the higher temperature necessary to operate a gas-oxy furnace… Fiber glass furnaces necessarily use chrome-based refractory products. Virtually all of the above-glass refractory in gas-oxy furnaces, unlike other furnace classes, is chrome-based refractory."[13]

Although all glass-melting furnaces are constructed using chromium refractories[14, 15] at and below the line of contact defined by the refractory wall and the molten glass within the glass-melting furnace (the glass/metal line), oxyfuel and some air-gas glass-melting furnaces have other glass-melting furnace parts constructed using chromium refractories, such as the crown and forehearth. The use of chromium refractories above the melt line is necessary to obtain the desired furnace life and reduce the necessity for hot repairs of the furnace. When the hot, corrosive and reactive gases of a gas-fired glass-melting furnace come in contact with the high-chromium refractories lining the area at and above the glass melt in high-temperature glass-melting furnaces, the chromium is available to be oxidized and converted into its hexavalent form.

In the stated opinion of the trade association (NAIMA, February 2012), oxyfuel furnaces have greater chromium emissions than other furnaces because "the combination of furnace design,

[10] "Oxygen Production" McGuineness, Rober M. and Kleinberg, William T. 1998. Oxygen-Enhanced Combustion. Charles E. Baukal, Jr. ed.
[11] US Department of Energy, Efficiency and Renewable Energy, Industrial Technologies Program, Final Technical Report, "Compressive Creep and Thermophysical Performance of Refractory Materials". Oak Ridge National Laboratory, June 2006, p. 9.
[12] The term gas-oxy, gas-oxyfuel, and oxyfuel are used interchangeably by the trade association. We are using the term "oxyfuel" here because it is the predominant term in the technical literature, and denotes a gas-fired furnace that uses oxygen in place of air in the natural gas-fired furnace.
[13] Comments of the North American Insulation Manufacturers Association on Behalf of the Wool Fiber Glass Manufacturers EPA's Proposed Rule National Emissions Standards for Hazardous Air Pollutants: Mineral Wool Production and Wool Fiberglass Manufacturing. Angus Crane and Granta Nakayama. February 3, 2012.

[14] Letter from NAIMA to U.S. EPA, January 28, 2013.
[15] Wool Fiberglass Manufacturing Industry Meeting Notes, August 31, 2011.

glass composition, higher flame temperatures, higher water vapor concentration, and an oxidizing atmosphere with increased concentration of oxides (filterable and condensable PM) can cause more rapid deterioration of the refractory in a gas-oxy fiber glass insulation manufacturing furnace than in other types of glass furnaces. The concentration of glass batch ingredient volatiles and water vapor in the oxyfuel furnace environment increases with the reduction in the flue gas volume (as compared to air gas furnaces, which dominated the industry prior to 1990). The peak flame temperatures are up to 40 percent higher than in air gas furnaces which increases the rate of melting, lowers the eutectic point, and drives the reaction of chromium from the trivalent (Cr_2O_3) state to the hexavalent (Cr_2O_6) state."

NAIMA, in their February 2012 letter, added that "the higher temperature of the gas-oxy burners can volatize the glass batch components more readily than in other furnaces. These glass volatiles that contain alkaline earth oxides reduce the temperature that chrome can be vaporized to as low as 1,832 degrees Fahrenheit. While the chrome must still reach temperatures of 2,700 degrees Fahrenheit to 2,900 degrees Fahrenheit to oxidize the trivalent chromium oxide (i.e., Cr_20_3 to Cr_20_6), the potentially increased volatiles can contribute to higher chrome emissions. The 40 percent higher peak flame temperature of oxyfuel burners also raises the probability that available chrome will encounter the conditions that will convert it to the hexavalent form (i.e., Cr_20_6). Combined, these differences generate conditions which are more corrosive to chrome refractory and can create favorable conditions for conversion to hexavalent chromium (Cr_20_6) inside a gas-oxyfueled furnace." According to NAIMA, "These severe conditions do not exist in the other fiber glass furnace classes." Note the flame temperature of the air-gas furnace is sufficient to convert chromium to the hexavalent state, and that the chromium emissions from air-gas furnaces is dependent upon the refractory materials used to construct the furnace at and above the glass melt line. [16]

[16] The flame temperature of the oxyfuel furnace is 5,000° F; the flame temperature of the air-gas furnace is 3,200-3,500° F.

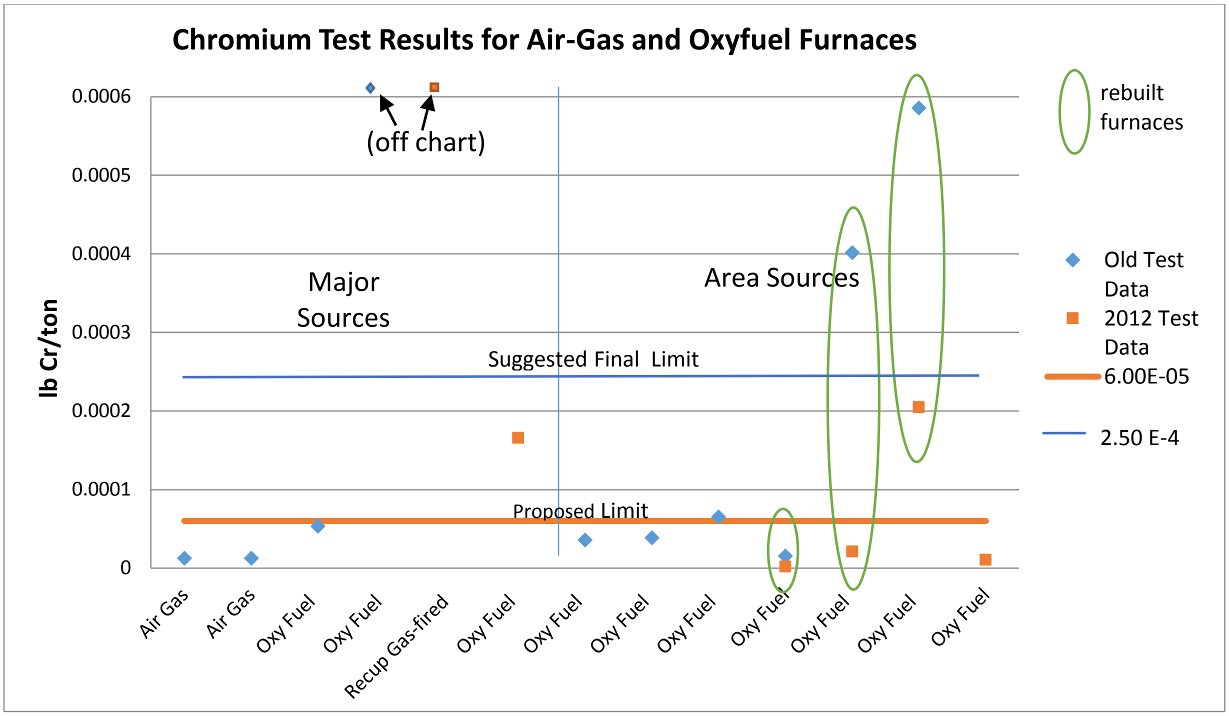


Figure 5. Chromium Test Results for Air-Gas and Oxyfuel Furnaces

CHEMISTRY OF GLASS AND ITS RELATION TO CHROMIUM EMISSIONS

As discussed by Brosnan, 2012[17], the wool fiberglass 'recipe' uses alkali or alkaline earth oxides, or boron oxide (borax) for its properties to terminate chains and sheets of silicon and oxygen tetrahedral in glass melt. The result of this ability to terminate is the formation of macromolecules. These macromolecules, kinetically unable to crystallize at low temperature, essentially polymerize the glass.

Other studies[18] advise us that, under normal industrial temperatures (which can exceed 1,300 ^{o}F) and oxidizing conditions, trivalent chromium, which is present in the refractory, oxidizes to hexavalent chromium.[19] The studies found that uncombined and available oxides were responsible for a higher yield of hexavalent chromium. Consequently, an increasing concentration of oxides in the oxyfuel glass-melting furnace environment increases the formation of chromium from the trivalent state to hexavalent state. The condition of high oxides in the oxyfuel glass-melting furnace environment is one characteristic of the highest emitting glass-melting furnace.[20]

[17] Technology Review. Chromium Emissions from Wool Fiberglass Melting Furnaces. Brosnan, Denis A. Ph.D., PE. Clemson University, Clemson, SC February 1, 2012.
[18] Metallurgical and Materials Transactions, Lee,Y., Nassaralla, C.L., 1998.
[19] Metallurgical and Materials Transactions B. "Minimization of Hexavalent Chromium in Magnesite-Chrome Refractory". Y. Lee and C. L. Nassaralla. Vol. 28 B, Oct. 1997-pp. 855-859.
[20] US EPA docket number EPA-HQ-OAR-2010-1042; document number 0067: Region 7 Notes on CertainTeed Kansas City. June 10, 2011. 13 pages.

According to Praxair, the formation of alkali vapors depends on furnace temperature, water vapor concentration and the flame characteristics. Additionally, Praxair compared the new oxyfuel furnace technology to the air-gas furnaces it replaced, and found that, "although the total amount of alkali volatilization, which is approximately proportional to the total particulate emissions, in an oxyfuel furnace, is less than that from the corresponding air fired furnace, the average concentration of the alkali species is increased by as much as three fold due to the elimination of nitrogen from the combustion air."

Brosnan further explains that chromium enters the glass in wool fiberglass furnaces below the glass line, and goes into solution without having the potential for volatilization at glass melting temperatures[21]. Chromium enters the silicate network structure of the glass as a 'modifier' of the network, and cannot form glass on its own due to thermodynamic constraints. According to Brosnan, chromium is held 'rigidly' in the silicate structure in interstices in the atomic network, and is present in coordinated complexes with oxygen[22].

Boron, a raw mineral additive required for the manufacture of wool fiberglass, is a highly reactive component of the wool fiberglass formula and interacts chemically with oxides in the furnace environment. Chromium refractory products have been developed for use with highly reactive and corrosive glasses.[23]

CHROMIUM EMISSIONS AS A FUNCTION OF REFRACTORY CORROSION

Both chemistry and temperature function as drivers in refractory corrosion. Brosnan[6] defined refractory corrosion as "refractory wear by loss of thickness and mass from the exposed face of the refractory ***as a consequence of chemical attack*** by a corroding fluid in a process in which the refractory and the corroding fluid react approaching chemical equilibrium in the zone of contact between the refractory and the fluid."[24] (emphasis added).

Brosnan describes refractory corrosion as the contact between the reactive component, or 'slag,' and the exposed surface of the refractory, or 'hot face,' at elevated temperature. Brosnan points to this interface as the driving mechanism for corrosion which continues throughout the life of the lining. Later in this work, Brosnan adds that "the hot face temperature primarily affects the rate of corrosion reactions….when the hot fact temperature is more than 20°C above the eutectic[25], corrosion is rapid." However, Brosnan adds that

[21] Chromium volatilization is only reported in the non-equilibrium melting of glasses at plasma processing temperatures, i.e., with flame temperatures typically reported as above 7,000°C (>12,000°F). Brosnan, 2012.
[22] C. Nelson, Transition Metal Ions in Glasses: Network Modifiers or Quasi-Molecular Complexes, Mat. Res. Bull. 18 (1983) 959-966.
[23] New High Chrome Fused Cast Refractory for Use in Contact with Highly Corrosive Glasses. T. A. Myles and F. Knee. American Ceramic Society Inc., Refractories Div., Sohio Engineered Materials Co., 1986.
[24] "Corrosion of Refractories", Brosnan, Denis A., Ph.D., P.E., Clemson University, Clemson, SC. in the Refractories Handbook, ed.2004. Charles A. Schacht. Marcel Dekker, Inc. NY, NY.

[25] The term **eutectic system**is used to describe a homogeneous solid mix of atomic and/or chemical species, to form a joint super-lattice, by striking a unique atomic percentage ratio between the components — as each pure component has its own distinct bulk lattice arrangement. It is only in this atomic/molecular ratio that *the eutectic system melts as a whole*, at a specific temperature (the eutectic temperature) *the super-lattice releasing at once all*

maintaining a hot face temperature of not more than 20°C above the solidus temperature between the slag and the refractory is impractical in many thick-wall refractory designs.

Corrosion of the refractory wall is further driven by slag penetration, which may result in both densification spalling and thermal shock spalling. Spalling (i.e., flaking or fragmenting) of the refractory wall increases the rate of refractory degradation.

Moreover, while the degradation of the glass-melting furnace refractory indicates increasing chromium emissions, that process does not necessarily follow a normal and predictable pattern. The degradation of refractories within the glass-melting furnace is a function of numerous factors, including temperature, time, stress and the composite effects of aging and creep response. These processes are highly nonlinear, so the traditional equations that assume steady-state deformation rates are not appropriate (DOE, 2006).

The facility with the highest emitting glass-melting furnace (an oxyfuel glass-melting furnace) submitted chromium testing over a single furnace campaign on four separate occasions over a 7-year period for state inventory reporting purposes. As shown in Table 4 below, those test results are extrapolated using permitted production rates to estimate annual emissions of chromium compounds. The estimated chromium emissions for 2004 are less than 5 pounds annually. Repeated chromium emissions testing for the state reports in 2005 and 2008 and permitted production rates for those years show chromium emissions increased to 540 pounds per year for the same glass-melting furnace. Emissions testing conducted in 2010 which speciated chromium by its compounds show that 93 percent of the chromium emitted was in the hexavalent state. This glass-melting furnace was not reconstructed during this 7-year period covered by the chromium testing.

Table 3. Summary of Chromium Emissions from 2004 – 2010 over a single furnace campaign.

Year	**Glass-Melting Furnace Chromium Emissions at Permitted Production Rate, Pounds per Year**
2004	<5
2005	30
2008	114
2010	540

its components into a liquid mixture. The eutectic temperature is the lowest possible melting temperature over all of the mixing ratios for the involved component species. Upon heating any other mixture ratio, and reaching the eutectic temperature, one component's lattice will melt first, while the temperature of the mixture has to further increase for (all) the other component lattice(s) to melt. Conversely, as a non-eutectic mixture cools down, each mixture's component will solidify (form its lattice) at a distinct temperature, until all material is solid. (Wikipedia, 2015).

We have also found that as the refractories of the gas-fired glass-melting furnaces degrade, the chromium of those refractories at and above the metal/glass line is emitted as particulate to the outside air. Chromium from the refractories below the metal/glass line is absorbed into the molten glass and becomes vitrified with the other raw minerals. Industry commented that refractory loss from degradation of the refractory walls in use is approximately 20,000 pounds of refractory annually[26]. However, much of the loss occurs below the glass melt line. The chromium released below the glass melt line is believed to mostly stay in the glass, although testing that would demonstrate this has not been found to date.

Figure 5. Chromium refractory wear pattern with furnace age, shown at rebuild. (Photo courtesy of Owens-Corning).

Table 3 shows that degradation of the chromium refractory resulted in a significant and exponential increase in chromium emissions during this period. One glass furnace manufacturer (Praxair, 2003) also corroborates that the rate of corrosion typically increases exponentially with temperature, but notes exceptions to this principle. Owens-Corning provided photos of the interior furnace refractory wall of a furnace that has been shut down for rebuild are shown in Figures 5-7. Note the curved quasi-hemispherical cavities typical of the wool fiberglass oxyfuel furnace interior. This pattern of refractory wear further supports the emissions profile as an exponential increase in chromium with furnace age.

[26] Minutes of the August 31, 2011 Meeting between US EPA and Representatives of the Wool Fiberglass Industry and NAIMA

The industry has a strong economic incentive to develop and use longer lasting refractories in construction of the glass-melting furnaces. Industry spokespersons have indicated that they rely on using chromium refractories offering longer glass-melting furnace life[27]. The cost of rebuilding a wool fiberglass glass-melting furnace ranges from $10-12 million; most of this cost is the cost of skilled labor (CertainTeed, 2011). While chromium refractories are more expensive than conventional refractories, they are only incrementally so (DOE, 2006). When conventional (high alumina/silica) refractories are used, the useful life of the glass-melting furnace is about 7 years. Use of chromium refractories to construct a wool fiberglass manufacturing oxyfuel furnace almost doubles its useful life when compared to other types of refractories.

Figure 6. Furnace wear of chromium refractories in a furnace under rebuild. The 'jade green' color is indicative of chromium refractory bricks. These chromium refractories are below, at, and above the glass line. (Photo courtesy of Owens-Corning).

New refractory technologies are being developed, tested, and placed into operation when viable to achieve longer furnace life. The development of fused-cast chromium refractories in 2000 made it possible to construct and operate oxyfuel furnaces over single campaigns of more than 12 years. Newer technologies, such as cast-in-place chromium refractories are expected to be implemented in the near future in some wool fiberglass furnaces.

[27] Email from Lauren.P.Alterman@saint-gobain.com to persons at the EPA, July 27, 2012, 10:32 am.

We collected source testing for all types of furnaces used in the wool fiberglass manufacturing industry. Specifically, each air-gas and oxyfuel furnace was tested, and facilities that operated identical electric furnaces provided testing for one furnace along with design, construction, and refractory information for all furnaces operated. Industry provided schematics of all types of furnace designs showing that while all wool fiberglass furnace 'tanks' (holding the molten materials) are constructed of high-chromium refractory, only the gas-fired furnaces are typically constructed from chromium refractories above the molten glass. Upon review of all the data submitted, we found that only gas-fired furnaces are designed in a manner that, during operation, may emit significant amounts of chromium compounds. Because the gas-fired furnaces are the only furnaces in which the chromium refractory is exposed to oxidizing conditions at temperatures exceeding 1,300 ^{o}F, gas-fired furnaces clearly demonstrate a greater potential for increased chromium emissions. While the highest emitting glass-melting furnace is located at a major source, note that the design and operation of gas-fired glass-melting furnaces is the same at major and area sources.

The thermal, physical and chemical properties of molten wool fiberglass cause corrosion and erosion to the refractory lining of the glass-melting furnace, and the glass-melting furnace must be constructed of materials capable of resisting this environment. Because oxygen burns very hot, some of the highest refractory performance requirements in the industry are placed upon wool fiberglass oxyfuel glass-melting furnaces.[28]

Figure 7. Note the spalling of the chromium refractory at and below the glass line. This is an air gas furnace that is being replaced by an oxyfuel furnace. (Photo courtesy of Owens-Corning).

[28] "New High Chrome Fused Cast Refractory for Use in Contact With Highly Corrosive Glasses", T.A. Myles and F. Knee, in Ceramic Engineering and Science Proceedings, The American Ceramic Society, 1986).

Consequently, an oxyfuel glass-melting furnace used to produce wool fiberglass must be constructed of high-chromium refractories because these are the only types of materials currently available that are suitable for this use and meet the rigorous practical demands of wool fiberglass manufacturing. The industry has commented that the use of high-chromium refractories is economically essential to wool fiberglass manufacturing. Because of the high thermal and chemical stressors in oxyfuel glass-melting furnaces under normal operations, high-chromium refractories are preferred by industry for economical and safe oxyfuel glass-melting furnace operation. Construction using these materials significantly increases the life of the glass-melting furnace. (Region 7, 2011; Saint-Gobain, 2012).

<u>CHROMIUM EMISSIONS INCREASE PROPORTIONAL TO CULLET USE</u>

The wool fiberglass industry has observed that chromium emissions increase with increasing use of cullet (ref). Cullet is waste glass, and may either be internal cullet or external cullet. The industry suggested that this may be due to chromium being released from the green glass portion of cullet upon remelting. However, according to other sources, once chromium has been added to a raw material mixture and melted to form a glass, it is not volatilized upon remelting. In their comments to the EPA's November 25, 2011 proposed RTR rule, NAIMA attached the comments from a technical advisor to the industry and the EPA[29]. Dr. Brosnan commented on the potential for chromium to be released upon remelting of the cullet in which it had been used as a colorant to impart a green color.

> *"Chromium is known as a constituent of glasses used for coloring purposes. Chromium enters the silicate network structure of the glass as a modifier' of the network, as it cannot form glass on its own due to thermodynamic constraints. As a modifier, any chromium in the glass is rigidly held in the silicate structure in interstices in the atomic network. Infrared spectroscopy now suggests the chromium is present in coordinated complexes with oxygen[30]. The result is that chromium is not volatiled from the glass at normal glass melting temperatures[31]. Chromium, which enters glass in (wool fiberglass) furnaces below the glass line, i.e., goes into solution, does not have potential for volatilization. Therefore, it is only potential volatilization from refractories at or above the glass line in furnaces that is of concern in this (Technology Review) report."*

The glass chemistry and mechanisms of chromium emissions suggest that chromium emission increase with increasing cullet use due to boride-driven reactivity in the furnace environment. Borides are a required ingredient in the wool fiberglass 'recipe', because the borides impart the properties needed to attenuate, or stretch, the molten glass into fibers that are flexible and springy when cooled. However, as previously stated (NAIMA, 2012; others…), the borides are highly reactive as a chemical species in the furnace environment. When raw minerals

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[29] Dr. Denis Brosnan of Clemson University, South Carolina. Technology Review. Chromium Emissions from Wool Fiberglass Melting Furnaces, February 1, 2012.

[30] C. Nelson, Transition Metal Ions in Glasses: Network Modifiers or Quasi-Molecular Complexes, Mat. Res. Bull. 18 (1983) 959-966.

[31] Chromium volatilization is only reported in the non-equilibrium melting of glasses at plasma processing temperatures, i.e., with flame temperatures typically reported as above 7000° C (>12,000° F).

predominate the raw material furnace feed mixture, oxides are readily released from those minerals upon the first melting (silicon dioxide, soda ash, etc.) These oxides react freely with the borides in the molten raw material mixture in the furnace environment. However, when cullet is used in place of all or most of the raw minerals, the mixture is starved of available reactants for the borides, and the borides will react with any available oxides. The most available oxide in the reactant-starved furnace environment are the chromium oxides of the refractory.

CONCLUSIONS

In summary, because of the advantages of oxyfuel glass-melting furnaces over other wool fiberglass glass-melting furnace technology described in the preceding discussions, oxyfuel glass-melting furnaces constructed of high-chromium refractories are expected to replace many existing wool fiberglass glass-melting furnaces of other designs (Letter from NAIMA to Ms. Susan Fairchild, EPA, January 28, 2013), particularly as sources of industrial oxygen are sited near wool fiberglass facilities. [32]

Consequently, electric glass-melting furnaces do not have the same potential to emit chromium compounds that gas-fired glass-melting furnaces have, and accordingly, many of the chromium test data collected at electric glass-melting furnaces are below the detection level of the emissions measurement method. All of the test data for electric glass-melting furnaces were also below the proposed chromium limit of 6×10^{-5} lb chromium per ton of glass pulled for glass-melting furnaces at major sources, as proposed by the EPA on November 25, 2011 (proposed RTR rule amendments). These data fall well below the final limit of 2.5 x 10-4 lb chromium per ton of glass pulled .

While the furnaces and control technologies are generally the same as those used at promulgation of the MACT standard in 1999, there have been some developments in furnace design and preference in control equipment[33]. Air-gas furnaces, once widely used throughout this industry, have been mostly phased out due to high nitrogen oxide (NOx) and PM emissions. In place of the air-gas furnace, oxyfuel furnaces are being constructed because they are more energy efficient, and because they emit NOx and PM at very low levels. Review of the industry literature[34,35,36,37,38] and public comments indicates that once a source of industrial oxygen is

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[32] Oxygen-Enhanced Combustion, Baukal, Charles E. Jr., Prince B. Eleazar III, and Bryan C. Hoke, Jr. 1998).

[33] From the EPA's Wool Fiberglass Manufacturing Technology Review Memorandum. Conducted under CAA section 112(d)(6) for chromium. June 2015.

[34] U.S. DOE Energy Efficiency and Renewable Energy, Industrial Technologies Program, Final Technical Report. "Compressive Creep and Thermophysical Performance of Refractory Materials". Oak Ridge National Laboratories. June 2006.

[35] Oxygen-Enhanced Combustion, Chapter 7. Baukal, Charles E., Jr. 1998.

[36] "Advances in Oxyfuel Fired Glass-Melting Technology". Hisashi Kobayashi. January 2004.

[37] "When Does Oxyfuel Make Sense?" Russell Hewertson, Combustion Technology, Air Products and Chemicals, Inc., 2005.

[38] Diagnostics And Modeling Of High-Temperature Corrosion Of Superstructure Refractories In Oxyfuel Glass Furnaces: Extended Superstructure Refractory Life Will Enhance Oxyfuel Firing Process. Elliott Levine, Office of Industrial Technologies Energy Efficiency and Renewable Energy, U.S. Department of Energy, December 2000.

sited in the vicinity of a wool fiberglass manufacturer, nearby facilities are likely to convert from air-gas or electric to oxyfuel technology.

While chromium refractories were used prior to 1999, the manufacturers of these products had not overcome some significant problems (such as spalling from thermal shock in certain high-temperature applications). As a result, their use was confined to limited areas of the furnace that typically experience low thermal shock or in areas where furnace repairs and refractory replacement could be performed readily. Developments in refractory technology and in furnace design are inextricably linked. Oxyfuel furnaces were not widely used prior to 1999 in the wool fiberglass industry, due to a number of factors, especially refractory degradation in the wool fiberglass furnace environment. The new technology at the time of an oxyfuel furnace constructed using conventional refractories of that time (e.g., alumina-silicate, zirconium) limited the furnace life to 4 or 5 years. With the advent of new refractory technology, life expectancy of new furnaces is expected to be significantly longer. With the industry focus upon new furnace designs and technology, the research to develop refractories that could withstand high temperatures, thermal shock and corrosive materials yielded the development of new types[39] of chromium refractory products that are used for construction of oxyfuel furnaces.

As a result, the wool fiberglass industry began a trend toward oxyfuel furnaces constructed using high-chromium refractory products, a trend that NAIMA noted is expected to continue into the future. This gives rise to increased chromium emissions as a result of both wool fiberglass raw material formulation (corrosivity) and associated refractory degradation (i.e., furnace wear). The EPA explained the mechanisms of chromium emissions at length in the April 15, 2011 proposal (78 FR 22379-22382) and in the Technology Review Memorandum for the Wool Fiberglass Manufacturing Source Category that accompanied the April 2013 notice.

DISPOSAL (RECYCLING) OF CHROMIUM REFRACTORY FROM THE FURNACE REBUILD

As has been discussed earlier, the EPA proposed a number of ways in which the wool fiberglass industry may reduce their chromium emissions. Use of a caustic (sodium hydroxide) scrubber at the outlet of the dry electrostatic precipitator (DESP), raw material substitution (i.e., decreased use of cullet with increased use of raw minerals), and rebuild of the furnace before the end of its useful life. This last option predominates in the industry at this time, as technological advances in furnace refractory are developing.

[39] Fused-cast chromium refractories and cast-in-place chromium refractories are among the types of chromium refractories in use in the wool fiberglass manufacturing industry since 2000.

Figure 8. A chromium refractory brick which is to be used in the rebuild of a new oxyfuel furnace. The development of very large refractory bricks with very smooth surfaces, extends furnace life by reducing the opportunity for glass breakthrough (‘ratholing’) at joints and brick to brick surfaces. (Photo courtesy of Owens-Corning).

The outside wall of the glass furnace may be reinforced with up to two layers of refractory blocks before the structural integrity of the furnace is threatened. After this point, when the interior of the furnace wall is eroded sufficiently to threaten breakthrough by the molten glass, the furnace is typically nearing the end of its useful life, and is scheduled for a rebuild.

Due to the toxicity of spent chromium refractories, wool fiberglass manufacturers must either dispose of the spent chromium refractory in accordance with RCRA Hazardous Waste requirements, or recycle these materials, which is typically conducted through the refractory manufacturer. Under RCRA (40 CFR Part 261), owners/operators with a material that meets the definition of Extraction Procedure (EP) Toxicity (that is, carrying a hazardous waste code) must conduct testing on the materials to determine their disposal. Some refractory materials contain chromium compounds as part of the refractory mixture. During operation, some of the chromium compounds will be converted into a hexavalent chromium. This means that the initial installation of the refractory material did not represent a health problem. However, when the refractory needed to be removed it presented a serious health problem. Therefore, when the refractory material is removed it creates a dust that may contain hexavalent chromium. As a result, inhaling the hexavalent chromium increases the risk of lung cancer and may also cause other health hazards.[40]

[40] ”Health and Safety Issues on Brick, Refractory and Insulation. Bases”, Gary J., Pres. BRIL, Inc. Copley, Ohio. 11th North American Waste to Energy Conference. 2003.

At least two manufacturers of chromium refractories offer a recycling option to their customers who have previously purchased these products for construction of their glass-melting furnaces. "As concerns about the environmental impact regarding the disposal of chrome refractories grew, NARCO took action and created the RESERV® Reuse Program to provide an alternative to treatment and hazardous waste land-filling for the glass maker." [41]

[41] In Glass Global Community, 2015 (online website news and advertisement). Harbison Walker International**.** North American Refractories Company. Cherrington Corporate Center, 400 Fairway Drive, 15108 Moon Township, PA.